

# PATENT SPECIFICATION

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## (54) PLATING PROCESS

(71) We, GEIGY (U.K.) LIMITED, a British Company, whose Registered Office address is Simonsway, Manchester, 22, Lancashire, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a novel method of depositing a metal layer on to a substrate and in particular to a method of depositing a metal layer on to a substrate firstly by an electroless plating process and subsequently by an electroplating process without removing the substrate from the plating solution.

Electroless plating solutions for producing ductile, bright layers of metals, particularly copper and nickel, on various substrates have long been known. In particular, there is increasing interest in electroless plating on to polymeric resin in predetermined patterns. Such electroless plating, however, provides only a layer of metal which is sufficiently thick to serve as an electrical conductor in subsequent electroplating on to the resin substrate. In order to deposit thicker layers of metal it has been necessary to transfer the substrate from the electroless plating solution to an electroplating solution.

We have now unexpectedly found that by carefully selecting the components of an electroless plating bath and by controlling the proportions of the said components, subsequent electroplating of an article may be carried out in the same solution used for electroless plating, without having to remove the component from the solution between the electroless and electroplating stages.

The use of the present invention offers several advantages over conventional processes. Operating the present invention requires only one plating bath and one rinse or wash bath, whereas conventional processes require at least four baths, namely an electroless plating bath,

a rinse bath, an electroplating bath, and a second rinse bath. Thus the process of the present invention involves a considerable saving in labour, space and capital equipment. Moreover, in known processes, when the substrate plated from the electroless plating bath is transported to an electroplating bath for further plating thereon, the danger exists of damaging the initial deposited layer by the mechanical handling. This is of particular importance when small components are barrel plated. In such conventional processes, any damage to the electroless deposit occurring during rinsing and transfer to the electroplating bath cannot be repaired and will result in unplated areas or areas of poor adhesion. When the processes of the present invention are used, however, any mechanical damage occurring even after electrodeposition has commenced, will be repaired by further electroless deposition. A further disadvantage of conventional processes is that in the case of copper plating, the copper deposit on the substrate formed in the electroless plating bath contains some copper oxide and may be further oxidised during transfer to the electroplating bath. This oxide can dissolve in many of the conventional electroplating baths such as acid copper sulphate or cyanide baths. This aerial oxidation and subsequent dissolution of oxide cannot happen in the processes of our invention. We have also found that the metal plating has a higher adhesion to the substrate when applied by the processes of our invention than when applied by the conventional processes.

According to the present invention, there is provided a process of plating a substrate comprising the electroless plating of a substrate by immersing the substrate in a bath comprising water, 0.002 to 0.60 moles per litre of a source of metal ions, 0.0015 to 6.0 moles of a complexing agent for the said metal ions, 0.002 to 2.5 moles of a reducing agent,

and thereafter electroplating on to the substrate whilst still immersed in the same bath.

The process of the present invention may be conveniently effected by completely immersing the substrate to be plated in the plating solution described hereinbefore. Desirably, during the initial electroless plating stage, the plating solution is agitated, for instance, by mechanical means or by air agitation. As soon as the electroless film is thick enough, that is of sufficient conductivity to carry the electroplating current without damage, the current may be applied. The time required for the deposition of an electroless film of sufficient thickness is normally of the order of 10 to 40 minutes. The process may be performed over a wide range of temperature while still maintaining the stability of the bath over long periods of time. In the case of copper plating baths, the preferred temperature limits are from 25° to 70°C., although temperatures above and below these limits may be employed if desired. For nickel plating baths on the other hand, the preferred temperature limits are higher, that is from 70° to 85°C., although in this case also operating temperatures above and below these limits may be used if so desired. As the temperature at which the plating bath is operated is increased, the rate at which the metal is deposited during the electroless stage is correspondingly increased and in addition higher cathode current densities may be employed during the electrolytic stage.

The substrate to be plated by the process of the present invention must be substantially completely free from grease and other contaminating material. Metallic substrates must be de-greased and freed from surface coatings such as oxide coatings in a conventional manner. Non-metallic substrates to be used in the process of this invention are preferably treated beforehand by any of the known processes for cleaning, sensitising, and activating such substrates, such as, treating the non-metallic substrate with a stannous chloride solution and subsequently with a palladium chloride solution.

After the above pre-treatment, the substrate is immersed in the electro/electroless plating solution of this invention and is left immersed until a metal deposit of reasonable thickness has been formed by the electroless plating process. The substrate is then made cathodic and electro-plated with the metal until the desired thickness of deposit has been obtained.

During the process of the present invention, the proportions of the metal ions and of the reducing agent gradually became depleted. Consequently, either continuously or periodically, the baths are regenerated in use by the addition of further amounts of these ingredients in sufficient quantities so as to maintain them within their optimum ranges.

The electroless deposition process is autocatalytic on many metals such as copper and nickel. Therefore during any idle period, electroless deposition will occur on the anodes. This may obviously be avoided by removing all the anodes from the solution during any such idle period, but if preferred, it may also be avoided by polarising the anodes so as to make them slightly anodic with respect to an inert electrode.

The anodes used in the plating baths of our invention can be any conventional electroplating anode, preferably of the metal being plated. For instance, for copper plating the anodes can be electrolytic copper sheet, rolled electrolytic copper, phosphorised copper, or oxygen-free high-conductivity (OFHC) copper.

Metals which may be deposited on to a substrate by means of the process of the present invention include for example cobalt, palladium, platinum, silver and gold, but the present process is particularly advantageous for use in the deposition of copper and nickel on to a substrate.

The metal complexing agent employed in the process of this invention may be any complexing agent for the metal to be deposited, the only limitation being that the complexing agent should perform satisfactorily in electroless and electroplating processes. Because of this obvious restriction the use of such complexing agents as Rochelle salt and alkali metal cyanides which are effective for electroless plating and electroplating processes respectively, is generally avoided.

Suitable complexing agents for use in the preferred copper and nickel plating processes include, for instance, amino-carboxylic acids, polyamino-polycarboxylic acids and alkali metal salts thereof, and alkylene and polyalkylene polyamines. Examples of suitable amino-carboxylic acids and polyamino-polycarboxylic acids and salts thereof include glycine, alanine, glutamic acid, ethylenediamine-tetra-acetic acid, the mono-, di-, tri- and tetra-alkali metal salts of ethylene diamine tetra-acetic acid, nitrilo-triacetic acid, hydroxyethyl-ethylenediamine-triacetic acid, and the tri-alkali metal salts of hydroxyethyl ethylenediamine-triacetic acid. Alkylene and polyalkylene polyamines which may be advantageously employed include, for instance, ethylene diamine, propylene diamine, diethylene diamine, triethylene tetramine, diethylene triamine and tetraethylene pentamine.

As specified hereinbefore, the proportion of the metal complexing agent should be within the range of from 0.0015 to 6.0 moles per litre of plating solution. Preferably, however, the complexing agent is present in an amount substantially in excess over the theoretical amount required to fully complex all the metal ions in the plating solution. The

preferred minimum excess of complexing agent is 100% by weight based on the weight of metal salt, the preferred maximum excess being restricted only by economic considerations. By having such a considerable excess of complexing agent present in the plating solution, we have found that the anodes are maintained in a clean state, whereas if an insufficient amount of complexing agent is present, the plating solution may become locally depleted of complexing agent at the anode, leading to undesirable precipitation of metal salts at and around the anode.

The plating solutions employed in the process of this invention must contain a reducing agent in order to operate the electroless deposition stage of plating. The reducing agent may be any of the conventional reducing agents such as formaldehyde, an alkali metal hypophosphite, an alkali metal borohydride or an amino borane. The concentration of reducing agent in the plating solution may be maintained at a constant level, or may be introduced only in sufficient quantity to electroless plate the quantity of substrate introduced at any one time. It is also possible to produce the necessary reducing agent electrolytically in the bath by electrolysis between subsidiary inert electrodes.

If copper is the metal to be deposited, the source of copper ions in the bath is preferably cupric sulphate, but other soluble salts for instance cupric nitrate, cupric chloride or cupric acetate also function satisfactorily. Advantageously, the proportion of cupric salt which is employed in the plating bath is within the range of from 0.005 to 0.4 moles per litre of plating solution.

The copper plating baths employed in the process of the present invention contain a reducing agent, for instance formaldehyde, an alkali metal borohydride such as sodium or potassium borohydride or an amino borane such as dimethyl or isopropyl amino borane. The proportion of the reducing agent, which is advantageously formaldehyde, is preferably within the range of from 0.03 to 1.5 moles per litre of plating solution, more preferably within the range of from 0.20 to 0.60 moles per litre of plating solution.

It is also known that the addition of certain additives may improve the quality of copper deposited from an electrolytic plating bath. In a preferred embodiment of the present invention, the process of this invention is effected employing a bath containing such known additives. Thus it is preferred in order to improve the stability of the bath during the process of the present invention that a sulphur compound is present in a proportion of less than 300 parts per million, preferably in a proportion of less than 1 part per million based on the plating solution. Suitable sulphur compounds include, for instance, thiourea, 2-mercaptobenzthiazole, methionine,

thioglycolic acid and sodium or potassium polysulphide.

In general, the copper plating baths employed in the process of the present invention additionally contain an alkali metal cyanide, preferably sodium or potassium cyanide, as a complexing agent for cuprous ions. The proportion of cyanide used may be within the range of from 0.0002 to 0.02 moles per litre but is more advantageously within the range of from 0.0002 to 0.001 moles per litre of plating solutions. The use of a cyanide complexing agent is preferred when the baths are to be used at lower temperatures, for example, temperatures of up to 35°C., but for higher bath temperatures, for instance within the range of from 35° to 65°C., we have found that superior results are achieved if a portion or, preferably, the whole of the cyanide component is replaced by an alkali metal carbonate such as sodium carbonate. The advantages of being able to work without cyanide are apparent, and if the alkali metal carbonate is used instead of cyanide, the preferred range of proportions of carbonate is from 0.1 to 0.4 moles per litre of plating solution.

The process of copper plating according to this invention is preferably effected by maintaining the pH value of the bath within the range of from 10 to 14 throughout the plating procedure.

In addition we have found that in order to achieve the optimum rate of anode corrosion and consequently the optimum rate of electroplating, it is particularly advantageous in the case of the copper plating bath to have present in the bath a hydroxycarboxylic acid, such as hydroxy-acetic acid, gluconic acid, hydroxymalonic acid and trihydroxy-glutaric acid, or an alkali of metal salt thereof, the particularly preferred acid being citric acid. The proportion of the hydroxycarboxylic acid present in the bath may be within the range of from 0.01 to 1.0 mole per litre, more preferably within the range of from 0.05 to 0.5 mole per litre of plating solution.

With respect to another preferred embodiment of the present invention, namely the electroless and electroplating of a substrate using a nickel bath for both processes, while nickel sulphate is the preferred salt for use in this process, nickel chloride or nickel acetate may be employed if desired. The use of crystalline, powdered salts is preferred since by this means greater bath stability is achieved.

In the process of the present invention using a nickel bath, it is advantageous to use an alkali metal hypophosphite as the reducing agent but the process is not restricted to the use of any particular reducing agent and other reducing agents such as alkali metal borohydrides or amino boranes may also be employed effectively. The proportion of reducing agent in the nickel plating bath employed in the process of this invention is

preferably within the range of from 0.15 to 1.20 moles per litre of plating solution. The preferred ratio of nickel ions to reducing agent in the plating solution is within the range of from 0.25 to 1.60:1.

The process of nickel plating according to this invention may be effected using a nickel plating bath which is either alkaline or acidic in nature. In general, nickel plating according to the method of this invention is carried out using a bath having a pH value within the range of from 4.0 to 9.0.

The nickel plating solution for use in the process of this invention may be stabilised, if desired, by the addition of a proportion of plumbous ions, for instance a proportion of a soluble plumbous salt within the range of from 1 to 10 parts per million. Alternatively, the nickel bath may be stabilised by the addition of a minor proportion, for example, up to 200 parts per million of arsenate ions. The arsenate anions may be conveniently introduced into the bath in the form of arsenic pentoxide.

The process of the present invention may be used for the plating of a wide variety of substrates. Suitable substrates include metals such as copper, nickel, steel, brass, chromium, tin and silver and non-metals, for example, glass, ceramic and polymeric materials, such as epoxy, amide, styrene, alkylene, especially ethylene and propylene, acrylic and vinyl polymer resins, and particularly acrylonitrile/butadiene/styrene (ABS) terpolymer resins which are finding increasing use in the manufacture of general car accessories. Components made of polymeric material which are particularly suitable for plating according to the process of this invention include those containing deeply recessed areas where conventional electroplating would not give deposits. In addition, the process of the present invention may be employed with advantage for the

plating and through-hole plating of printed circuits. By means of the process of this invention, metal deposits on ABS polymers of excellent adhesion values have been obtained, these values being substantially in excess of values obtained by conventional plating processes.

The present invention is further illustrated by the following Examples.

#### EXAMPLE 1

Plastic sheet moulded from the acrylonitrile/butadiene/styrene (ABS) terpolymer sold under the trade mark Cynolac EP. 3510 was cleaned by immersion for two minutes in a solution of 8 oz. per gallon of an alkaline cleaner (Enplate PC-452) at 140°F. and then rinsed with cold water. The sheet was then neutralised by immersion for 15 seconds in a solution of 8 oz. per gallon of an acidic pH buffer solution (Enplate AD-480) at room temperature and then again rinsed with cold water. The sheet was then conditioned for 5 minutes in Enplate Conditioner 470 (believed to be a dilute chromic acid solution) at 120°F., rinsed with warm water, neutralised by immersion for 15 seconds in a solution of Enplate AD-480 as before and rinsed in cold water. Next the sheet was sensitised by immersion for 15 seconds in a solution of 1 part of Enplate Sensitiser 432 (believed to be based on stannous chloride and hydrochloric acid) to 15 parts of water at room temperature, rinsed twice with cold water, activated by immersion for 15 seconds in a solution of 1 part of Enplate Activator 440 (an acid solution of a noble metal salt) to 15 parts water at room temperature and finally rinsed thoroughly with cold water. (Enplate is a trade mark). After this pretreatment the ABS parts were immersed in the following bath at 23°C with agitation of the solution:—

85	Copper sulphate	5 grams	(0.02 moles)
	Di-sodium ethylenediamine		
	tetra-acetic acid	18.6 grams	(0.05 moles)
	Sodium hydroxide	9.15 grams	(0.229 moles)
	Formaldehyde (36% weight/weight aqueous solution)	27.7 millilitres	(0.326 moles)
90	Sodium cyanide	0.0229 grams	(0.000468 moles)
			(22.9 parts per million)
	Water	to make	
		1 litre	

The pH value of the bath was adjusted to 12.1 with 50% weight/volume aqueous sodium hydroxide solution.

After immersion for 15 minutes, a deposit of copper had formed on the ABS which was sufficiently thick to be electrically conductive and to carry the current necessary for electroplating without burning at the points of electrical contact. Electrolytic deposition of copper was then commenced by making the ABS cathodic, using a cathode current density of

2 amps/square foot for the first two minutes and increasing this to 10 amps/square foot for a further two minutes. The anode current density was maintained within the range of from 10 to 15 amps/square foot throughout the electroplating stage.

The copper deposit obtained had a thickness of 0.000025 inches and was bright and ductile. The deposit was suitable for further finishing by electroplating with other metals such as nickel or chromium if desired.

The adhesion of the copper deposit to the ABS was measured by determining the peel strength, and value on excess of 18 pounds/linear inch were obtained. For the purpose of comparison, a similar ABS polymer sheet was given the same pretreatment but was then plated in "Enthone CU400" electroless copper plating solution followed by electroplating in a separate acid copper sulphate bath. The peel strength obtained on this sample of plated ABS was only 9—13

pounds/linear inch. Thus it can be seen that the plating process of the present invention as well as being more convenient to use, also gives a greatly improved adhesion of the deposit on to the substrate.

#### EXAMPLE 2

A sheet of stainless steel which had been de-greased and treated with acid to remove any oxide coating, was immersed in a bath consisting of:—

	Copper sulphate	5 grams	(0.02 moles)
	Dio-sodium ethylenediamine		
	tetra-acetic acid	18.6 grams	(0.05 moles)
25	Sodium citrate	20 grams	(0.068 moles)
	Sodium hydroxide	14.32 grams	(0.358 moles)
	Formaldehyde (36% weight/weight aqueous solution)	27.5 millilitres	(0.329 moles)
	Sodium cyanide	0.0229 grams	(0.000468 moles)
30	Water	to make one litre	(22.9 parts/million)

The plating was carried out as in Example 1 and a similar bright, ductile copper deposit was obtained on the stainless steel.

#### EXAMPLE 3

An ABS (Cycloc EP 3510) polymer base sheet was pretreated with a cleaner, neutraliser, conditioner, sensitizer and activator as specified in Example 1. The ABS parts were then immersed in the following bath:—

	Copper sulphate	5 grams	(0.02 moles)
	Di-sodium ethylenediamine		
40	tetra-acetic acid	53.5 grams	(0.144 moles)
	Sodium hydroxide	24.4 grams	(0.61 moles)
	Formaldehyde (as 36% weight/weight aqueous solution)	106.5 millilitres	(1.28 moles)
45	Sodium cyanide	0.2 grams	(0.0041 moles)
	Water	to make one litre	(200 parts per million)

The pH value of the bath was adjusted to 12.7 using 15% weight/volume aqueous sodium hydroxide solution.

The plating was carried out as in Example 1 and a similar bright, ductile copper deposit was obtained.

Further ABS parts were plated in the same solution until the plating solution had been in continuous use for 5 hours. The plating solution was then replenished by adding —ths of

the original quantity of copper sulphate, —th

the quantity of formaldehyde and —th

the quantity of sodium cyanide, the pH value being re-adjusted with sodium hydroxide solution. More ABS components were then plated in the replenished solution for a further 5 hours before replenishment was again necessary. This replenishment procedure was re-

peated six times without any evidence of deterioration of the plating solution.

#### EXAMPLE 4

A sheet of stainless steel which had been de-greased and treated with acid to remove any oxide coating was immersed in a bath consisting of:—

	Copper sulphate	5 grams
	Di-sodium ethylenediamine	
	tetra-acetic acid	68.8 grams
75	Sodium hydroxide	17.2 grams
	Formaldehyde (as 36% weight/weight aqueous solution)	28.6 millilitres
	Sodium cyanide	0.0229 grams
80	Thiourea	0.0002 grams
	Water	to make 1 litre

The pH value of the bath was adjusted to 12.7 using 50% weight/volume aqueous sodium hydroxide solution.

The plating was carried out as in Example

1. A bright, ductile copper deposit was obtained on the stainless steel.

Further stainless steel parts were plated in the same solution until the plating solution had been in continuous use for 5 hours. The plating solution was then replenished by adding

$\frac{3}{5}$ ths of the original quantity of copper

sulphate,  $\frac{1}{10}$ th the quantity of formaldehyde

and  $\frac{1}{100}$ th the quantity of sodium cyanide,

the pH being re-adjusted with sodium hydroxide solution. More stainless steel components were then plated in the replenished solution for a further 5 hours before replenishment was again necessary. The replenishment procedure was repeated six times without any evidence of deterioration of the plating solution.

#### EXAMPLE 5

A sheet of stainless steel which had been de-greased and treated with acid to remove any oxide coating was immersed in the following bath:—

	Copper sulphate	5 grams	(0.02 moles)
	Di-sodium ethylenediamine		
	tetra-acetic acid	53.5 grams	(0.144 moles)
25	Sodium hydroxide	18.3 grams	(0.457 moles)
	Formaldehyde (as 36% weight/weight aqueous solution)	60 millilitres	(0.72 moles)
30	Sodium cyanide	0.091 grams	(0.00186 moles, 91 parts per million).
	2-Mercaptobenzthiazole	0.0002 grams	(0.2 parts per million)
	Water	to make 1 litre	

The pH value of the bath was adjusted to 12.4 using 10% weight/volume aqueous sodium hydroxide solution.

The plating was carried out as in Example 1 except that a temperature of 50°C. was used.

The copper deposits obtained had a thickness of 0.0000375 inches and was bright and ductile.

Solution replenishment as described in Example 3 was carried out without any deterioration in performance of the plating solution.

#### EXAMPLE 6

An ABS (Cyclac EP 3510) polymer base sheet was pretreated as described in Example 1 and was then immersed in the following solution:—

	Copper sulphate	5 grams	(0.02 moles)
	Di-sodium ethylenediamine		
	tetra-acetic acid	53.5 grams	(0.144 moles)
55	Sodium hydroxide	13.75 grams	(0.344 moles)
	Formaldehyde (as 36% weight/weight aqueous solution)	40 millilitres	(0.48 moles)
	Sodium carbonate	42.8 grams	(0.405 moles)
60	2-Mercaptobenzthiazole	0.001 grams	(1 part per million)
	Water	to make 1 litre	

The pH value of the bath was adjusted to 11.8 using 50% weight/volume aqueous sodium hydroxide solution.

After 15 minutes immersion at 50°C. a deposit of copper had formed on the ABS which was sufficiently thick to be electrically conductive and to carry the current necessary for electro-plating without burning at the points of electrical contact. Electro deposition of copper was then commenced by making the ABS cathodic, using a cathode current density of 2 amps/square foot for the first two minutes and increasing this to 10 amps/square foot for a further 30 minutes. An anode current density of 10 to 15 amps/square foot was used.

The copper deposit obtained had a thickness of 0.000563 inches and was bright and ductile.

The plating solution was used for 5 hours for plating ABS using the above plating cycle. The solution was then replenished as described in Example 3 and the process repeated six times without any evidence of deterioration of the solution.

#### EXAMPLE 7

An ABS (Cyclac EP 3510) polymer base sheet was pretreated as described in Example 1 and was then immersed in a bath consisting of:—

5	Nickel chloride	21.4 grams	(0.09 moles)
	Di-sodium ethylenediamine		
	tetra-acetic acid	14.9 grams	(0.04 moles)
	Sodium hypphosphite	19.8 grams	(0.225 moles)
	Lead chloride	0.4 grams	
	Water	to make one litre	

The pH value of the bath was adjusted to 4.5 with 50% weight/volume aqueous sodium hydroxide solution.

10 After 30 minutes immersion at 70°C., an electroless nickel deposit of sufficient thickness to permit electro-plating was obtained. Further nickel was then electro deposited on the ABS by making the ABS cathodic, using a cathode current density of 10 amps/square foot for 30 minutes. The anode current density was 10 amps/square foot.

The nickel alloy deposit obtained was bright and ductile and had a thickness of approximately 0.00044 inches and it was suitable for further plating if required.

The sodium hypophosphite was continuously replenished by the dropwise addition of 100 millilitres/hour of 0.45 M sodium hypophosphite solution. After 3 hours continuous use

the plating bath was replenished with  $\frac{1}{10}$ -th

of its original nickel content by the addition of 200 mls of 0.5 M  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  solution

and with  $\frac{1}{10}$ -th of its original lead content by

the addition of 20 mls of 2 grams/litre  $\text{PbCl}_2$  solution, and the pH value of the bath was adjusted with 50% weight/volume aqueous sodium hydroxide solution.

Nickel plating was continued for a further 3 hours and the solution was again replenished as described above. The process was repeated altogether six times. No decomposition of the bath occurred. The coatings on the ABS continued to be smooth and bright.

#### EXAMPLE 8

A stainless steel sheet which had been degreased and treated with acid to remove any oxide coating was immersed in a bath consisting of:—

45	Nickel chloride	21.4 grams	(0.09 moles)
	Di-sodium ethylenediamine		
	tetra-acetic acid	14.9 grams	(0.04 moles)
	Lead chloride	0.04 grams	
50	Sodium hypophosphite	39.6 grams	(0.45 moles)
	Water	to make one litre	

The pH value of the bath was adjusted to 4.5 with 50% weight/volume aqueous sodium hydroxide solution.

Plating was carried out in a similar manner to that described in Example 7 except that a temperature of 85°C was used throughout. The nickel alloy deposit obtained was bright and ductile and had a thickness of 0.00058 inches. It was suitable for further electro-plating if this was required.

British Patent No. 1041975 describes and claims a bath for the electroless plating of copper which contains: a water soluble copper salt, a complexing agent for cupric ion, an alkali metal hydroxide, formaldehyde and a small effective amount of a sulfur compound sufficient and capable of stabilizing the bath the amount of sulphur-compound added being insufficient to render the bath non-auto-catalytic.

British Patent No. 910709 describes and claims a bath for the electroless plating of copper which contains: water, and water-soluble copper salt, from 0.002 to 0.15 moles; a copper complexing agent, from 0.5 to 2.5 times the moles of the copper salt; an alkali-metal hydroxide, to give a pH of from 10.5 to 14; formaldehyde, from 0.06 to 3.4 moles;

and a soluble inorganic cyanide, from 0.00002 to 0.06 moles.

#### WHAT WE CLAIM IS:—

1. A process of plating a substrate comprising the electroless plating of a substrate which is substantially completely free from grease and other contaminating material by immersing the substrate in a bath comprising water, 0.002 to 0.60 moles per litre of a source of metal ions, 0.0015 to 6.0 moles of a complexing agent for said metal ions 0.002 to 2.5 moles of a reducing agent, and thereafter electroplating on to the substrate whilst still immersed in the same bath.

2. A process as claimed in claim 1 wherein the substrate is non-metallic and is treated with a stannous chloride solution and subsequently with a palladium chloride solution prior to immersion in the plating solution.

3. A process as claimed in claim 1 or 2 wherein the plating solution is agitated during the initial electroless plating stage.

4. A process as claimed in any of the preceding claims wherein the electroless deposition of metal is continued until the deposited metal film is of sufficient thickness to

carry the electroplating current without damage to the film.

- 5 A process as claimed in claim 4 wherein the time period for electroless deposition of metal is within the range of from 10 to 40 minutes.

- 6 A process as claimed in any of the preceding claims wherein after the electroless plating stage, the substrate is made cathodic and electro-plated until the desired thickness of metal deposit has been obtained.

- 7 A process as claimed in any of the preceding claims wherein the proportions of the metal ions and of the reducing agent are maintained during the process by periodic additions in sufficient quantities to maintain them within their optimum ranges.

- 8 A process as claimed in any of the preceding claims wherein the complexing agent is an amino-carboxylic acid, a poly-amino-polycarboxylic acid or an alkali metal salt of either of these acids, or an alkylene- or polyalkylene-polyamine.

- 9 A process as claimed in claim 8 wherein the amino-carboxylic, the polyamino-carboxylic acid or the alkali metal salt thereof is glycine, alanine, glutamic acid, ethylene diamine-tetra-acetic acid, the mono-, di-, tri- and tetra-sodium salts of ethylene diamine tetra-acetic acid, nitrilo tri-acetic acid, hydroxyethyl-ethylene-diamine tri-acetic acid or the tri-alkali metal salt of hydroxyethyl ethylene-diamine-tri-acetic acid.

- 10 A process as claimed in claim 8 wherein the alkylene- or polyalkylene-polyamine is ethylene diamine, propylene diamine, diethylene diamine, triethylene tetramine, diethylene triamine or tetra-ethylene pentamine.

- 11 A process as claimed in any of the preceding claims wherein the complexing agent is present in an amount substantially in excess over the theoretical amount required to fully complex all the metal ions in the plating solution.

- 12 A process as claimed in claim 11 wherein the minimum excess amount of complexing agent is 100% by weight based on the weight of metal salt.

- 13 A process as claimed in any of the preceding claims wherein the reducing agent is formaldehyde, an alkali metal hypophosphite, an alkali metal borohydride or an amino borane.

- 14 A process as claimed in any of the preceding claims wherein the substrate is a metal.

- 15 A process as claimed in claim 14 wherein the metal is copper, nickel, steel, brass, chromium, tin or silver.

- 16 A process as claimed in any of claims 1 to 13 wherein the substrate is non-metallic.

- 17 A process as claimed in claim 16 wherein the substrate is glass or ceramic material.

- 18 A process as claimed in claim 16 wherein the substrate is an epoxy, amide,

styrene, ethylene, propylene, acrylic or vinyl polymer.

- 19 A process as claimed in claim 16 wherein the substrate is an acrylonitrile/butadiene/styrene terpolymer resin.

- 20 A process as claimed in any of the preceding claims wherein the metal deposited on to the substrate is copper.

- 21 A process as claimed in claim 20 wherein the anodes are of electrolytic copper sheet, rolled electrolytic copper, phosphorised copper, or oxygen-free high-conductivity copper.

- 22 A process as claimed in claim 20 or 21 wherein the process is effected at a bath temperature within the range of from 25° to 70°C.

- 23 A process as claimed in any of claims 20 to 22 wherein the source of copper ions is cupric nitrate, cupric chloride or cupric acetate.

- 24 A process as claimed in any of claims 20 to 22 wherein the source of copper ions is cupric sulphate.

- 25 A process as claimed in any of claims 20 to 24 wherein the proportion of cupric salt in the plating bath is within the range of from 0.005 to 0.4 moles per litre of plating solution.

- 26 A process as claimed in any of claims 20 to 25 wherein the reducing agent is formaldehyde.

- 27 A process as claimed in any of claims 20 to 26 wherein the proportion of reducing agent is within the range of from 0.03 to 1.5 moles per litre of plating solution.

- 28 A process as claimed in claim 27 wherein the proportion of reducing agent is within the range of from 0.20 to 0.60 moles per litre of plating solution.

- 29 A process as claimed in any of claims 20 to 28 wherein the copper plating bath contains a sulphur compound in a proportion of less than 300 parts per million of plating solution.

- 30 A process as claimed in claim 29 wherein the copper plating bath contains a sulphur compound in a proportion of less than 1 part per million of plating solution.

- 31 A process as claimed in claim 29 or 30 wherein the sulphur compound is thiourea, 2-mercaptobenzthiazole, methionine, thioglycolic acid, sodium polysulphide or potassium polysulphide.

- 32 A process as claimed in any of claims 20 to 31 wherein the process is operated at a temperature of up to 35° and the copper plating bath contains an alkali metal cyanide.

- 33 A process as claimed in claim 33 wherein the alkali metal cyanide is sodium or potassium cyanide.

- 34 A process as claimed in claim 33 or 34 wherein the proportion of cyanide is within the range of from 0.0002 to 0.02 moles per litre of plating solution.



35. A process as claimed in claim 35 wherein the proportion of cyanide is within the range of from 0.0002 to 0.001 moles per litre of plating solution.
- 5 36. A process as claimed in any of claims 21 to 32 wherein the process is operated at a temperature within the range of from 35° to 65°C and the copper plating bath contains an alkali metal carbonate.
- 10 37. A process as claimed in claim 37 wherein the alkali metal carbonate is sodium carbonate.
38. A process as claimed in claim 37 or 38 wherein the proportion of carbonate is within the range of from 0.1 to 0.4 moles per litre of plating solution.
- 15 39. A process as claimed in any of claims 20 to 38 wherein the pH value of the bath is maintained within the range of from 10 to 14, throughout the plating procedure.
- 20 40. A process as claimed in any of claims 20 to 39 wherein the copper plating bath contains a hydroxycarboxylic acid or an alkali metal salt thereof.
- 25 41. A process as claimed in claim 40 wherein the hydroxy carboxylic acid or alkali metal salt thereof is hydroxy-acetic acid, gluconic acid, hydroxy-malonic acid or trihydroxy glutaric acid or an alkali metal salt of said acids.
- 30 42. A process as claimed in claim 40 wherein the hydroxycarboxylic acid is citric acid.
43. A process as claimed in any of claims 40 to 42 wherein the proportion of hydroxycarboxylic acid is within the range of from 0.01 to 1.0 mole per litre of plating solution.
- 35 44. A process as claimed in claim 43 wherein the proportion of hydroxycarboxylic acid is within the range of from 0.05 to 0.5 mole per litre of plating solution.
- 40 45. A process as claimed in any of claims 1 to 19 wherein the metal deposited on to the substrate is nickel.
46. A process as claimed in claim 45 wherein the source of nickel ions is nickel chloride or nickel acetate.
- 45 47. A process as claimed in claim 45 wherein the source of nickel ions is nickel sulphate.
48. A process as claimed in claim 46 or 47 wherein the source of nickel ions is added to the bath in the form of a crystalline, powdered salt.
- 50 49. A process as claimed in any of claims 45 to 48 wherein the reducing agent is an alkali metal hypophosphite.
- 55 50. A process as claimed in any of claims 45 to 49 wherein the proportion of reducing agent in the nickel plating bath is within the range of from 0.15 to 1.20 moles per litre of plating solution.
- 60 51. A process as claimed in any of claims 45 to 50 wherein the proportion of nickel ions to reducing agent in the plating solution is within the range of from 0.25 to 1.60:1.0.
- 65 52. A process as claimed in any of claims 45 to 51 wherein the pH value of the bath is maintained within the range of from 4.0 to 9.0.
53. A process as claimed in any of claims 45 to 52 wherein the nickel plating solution contains a proportion of plumbous ions.
- 70 54. A process as claimed in claim 53 wherein the plumbous ions are present in the form of a soluble plumbous salt in a proportion within the range of from 1 to 10 parts per million of plating solution.
- 75 55. A process as claimed in any of claims 45 to 52 wherein the nickel plating solution contains a proportion of arsenate ions.
- 80 56. A process as claimed in claim 55 wherein the arsenate ions are present in a proportion of up to 200 parts per million of plating solution.
57. A process as claimed in claim 55 or 56 wherein the arsenate ions are introduced into the bath in the form of arsenic pentoxide.
- 85 58. A process of plating a substrate substantially as described in any of the Examples.
59. A metal-plated substrate whenever produced by a process as claimed in any of the preceding claims.
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